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INTERNAL REPORT

APPLICATION OF THE METHOD OF THE AUXILIARY MATRIX IN EVALUATING

VIRIAL COEFFICIENTS FROM PVT DATA

BY

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## HELIUM RESEARCH CENTER

### INTERNAL REPORT

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APPLICATION OF THE METHOD OF THE AUXILIARY MATRIX IN EVALUATING VARIOUS  
COEFFICIENTS FROM DATA<sup>1/</sup>

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minants and is most desirable for most calculation work as the only writing involved is that of writing the auxiliary matrix and the final results.

This report gives a brief summary of the method of the auxiliary matrix, previously published by Grout, and its application to rational, integral functions of one to four degrees together with formulas for evaluating the standard error in a single measurement, the standard error in each coefficient, and the standard error of these functions.

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The formulas presented in this report for evaluating the standard  
APPLICATION OF THE METHOD OF THE AUXILIARY MATRIX IN EVALUATING VIRIAL  
coefficients mentioned above the elements of the

auxiliary matrix. These formulas were derived by expressing the  
constants in terms of the original data and applying the law for the

"Propagation of Errors", in which the error assigned to each of the  
observed measurements.

#### INTRODUCTION

#### ABSTRACT

In a previous publication the author has presented formulas for eval-  
uating the standard error in a single measurement, the standard error in each coefficient, and the standard error of these functions of one to four degrees together with formulas for evaluating the standard error in a single measurement, the standard error in each coefficient, and the standard error of these functions.

An important application of the method of the auxiliary matrix is in the least squares evaluation of virial coefficients from PVT data. This analytical method for solving constants from general equations containing these coefficients is much shorter than a solution by determinants and is most desirable for desk calculation work as the only writing involved is that of writing the auxiliary matrix and the final results.

This report gives a brief summary of the method of the auxiliary matrix, previously published by Crout, and its application to rational, integral functions of one to four degrees together with formulas for evaluating the standard error in a single measurement, the standard error in each coefficient, and the standard error of these functions.

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The formulas presented in this report for evaluating the standard errors mentioned above are expressed in terms of the elements of the auxiliary matrix. These formulas were derived by expressing the constants in terms of the original data and applying the law for the "Propagation of Errors", unit weight being assigned to each of the observed measurements.

## INTRODUCTION

In a previous publication (3)<sup>2/</sup>, formulas were presented for eval-

2/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

uating the constants of rational integral functions of one to four degrees together with formulas for calculating the standard error of a single measurement, the standard error in each coefficient, and the standard error of the resulting function. The derivations for calculating the errors mentioned above were based on the law for the "Propagation of Errors" (1, 4), unit weight being given to each of the observed measurements.

After publication, this author became aware of the Crout Method (2), the method of the auxiliary matrix. This method is a modification of the elimination method and it is most desirable for desk calculation work. It is a fact that this analytical method for solving a set of normal equations is much shorter than a solution by determinants as solution using the Crout method.



given previously (3). Therefore, it was decided to derive the equations for evaluating the above-mentioned errors. This author does not claim any originality with respect to this method for solving constants from general equations containing these coefficients.

The purpose of this report is to give, without proof, the Crout Method as applied to rational, integral functions of one to four degrees together with formulas which I have derived for evaluating the standard error in a single  $Y_i$ , in each coefficient, and in the resulting function. The formulas presented for evaluating these errors are expressed in terms of the elements of the auxiliary matrix and they were derived on the basis of the law for the "Propagation of Errors", each observation having unit weight.

#### CALCULATION OF THE STANDARD ERROR

An important application of the method of the auxiliary matrix is in the least squares evalation of the coefficients from a general equation containing these constants. For example, the PV product of a gas is represented as a function of either the pressure or the density by an equation such as

$$Y = A + Bx_1 + Cx_2 + Dx_3 + Ex_4 + \dots$$

in which  $Y$  is the PV product;  $x_1, x_2, x_3, x_4, \dots$  are forms of either the pressure or the density variable; and  $A, B, C, D, E, \dots$  represent so-called virial coefficients to be determined by least squares solution using the Crout method.



The form of the general equation given above is desirable when considered from the standpoint of the independent variable. That is, the PV-dependent variable may or may not be expressed in terms of a power series expansion

$$x = x_1; x^2 = x_2; x^3 = x_3; x^4 = x_4; \dots$$

of the independent variable.

The following symbolism has been used in the derivation of all equations for evaluating standard errors contained in this report:

$y_i, x_{1i}, x_{2i}, \dots$  designate observed values;  $Y$  refers to the function;

$s_A^2, s_B^2, \dots$  are the variances in the coefficients;  $s_{Y_i}^2$  and  $s_{Y_i}$  are the variance and the standard error in a single  $y_i$ , respectively;  $s_Y^2$  and

$s_Y$  are the variance and the standard error in the function, respectively;  $R$  and  $C$  represent the words row and column, respectively, and refer to those elements of the given coefficient matrix; and  $r$  and  $c$  represent the words row and column, respectively, and refer to those elements of the auxiliary matrix.

Now if one has a function,  $F$ , of a number of independently observed quantities,  $y_1, y_2, y_3, \dots$ , whose standard errors  $s_{Y_1}, s_{Y_2}, s_{Y_3}, \dots$  are known, then the variance,  $s_F^2$ , in  $F$  is given by the formula (1, 4) for the "Propagation of Errors":

$$s_F^2 = \left( \frac{\partial F}{\partial y_1} \cdot s_{Y_1} \right)^2 + \left( \frac{\partial F}{\partial y_2} \cdot s_{Y_2} \right)^2 + \dots + \left( \frac{\partial F}{\partial y_n} \cdot s_{Y_n} \right)^2 \quad (1)$$

the summation being over  $i$  for 1 to  $n$  for the  $n$  observations. Taking the partial derivative of equation (5) with respect to first  $A$  and



Extracting the square root of the variance, one obtains a value on the same scale as the original measurements; this value is called the standard error or standard deviation.

Suppose we have a function of the kind

$$Y = A + Bx_1 \quad (2)$$

where A and B are to be evaluated by least squares solution (using the method of the auxiliary matrix) along with the following errors: the standard error of a single measurement; the standard error in each coefficient; and the standard error of the resulting function. The estimated variance,  $s_{Y_i}^2$ , of a single  $Y_i$  is given as

$$s_{Y_i}^2 = \frac{\sum(Y_i^{\text{obs}} - Y_i^{\text{cal}})^2}{n - 2} \quad (3)$$

Now in order to evaluate the standard error in both intercept and slope, we must express these quantities in terms of the original data. The residuals,  $w_i$ , are

$$w_i = (Y_i - A - Bx_{1i}) \quad (4)$$

and the sum of the squares of the residuals is

$$\sum w_i^2 = \sum (Y_i - A - Bx_{1i})^2 \quad (5)$$

the summation being over i for 1 to n for the n observations. Taking the partial derivative of equation (5) with respect to first A and



then B and setting each derivative equal to zero gives the normal equations

$$(Y_1 - A - Bx_{11}) + \dots + (Y_n - A - Bx_{1n}) = 0 \quad (6)$$

$$x_{11} (Y_1 - A - Bx_{11}) + \dots + x_{1n} (Y_n - A - Bx_{1n}) = 0 \quad (7)$$

and our final results are

or their equivalents

$$An + B\sum x_{1i} = \sum Y_i \quad (8)$$

$$A \sum x_{1i} + B\sum x_{1i}^2 = \sum x_{1i} Y_i \quad (9)$$

Now equations (8) and (9) can be written as a general coefficient matrix as

$$\begin{vmatrix} n & \sum x_{1i} & \sum Y_i \\ \sum x_{1i} & \sum x_{1i}^2 & \sum x_{1i} Y_i \end{vmatrix} \quad (\text{Matrix 10})$$

or, abbreviating the above, using the letters R and C to represent the words row and column, respectively, as

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 \end{vmatrix} \quad (\text{Matrix 11})$$

where  $R_1 C_1 = n$ ;  $R_1 C_2 = \sum x_{1i}$ ;  $R_1 C_3 = \sum Y_i$ ;  $R_2 C_1 = \sum x_{1i}$ ;  $R_2 C_2 = \sum x_{1i}^2$ ; and

$R_2 C_3 = \sum x_{1i} Y_i$ . The solution of the constants of equation (2) requires



that we evaluate an auxiliary matrix and a final result. Now our auxiliary matrix is of the form

1. Rules for obtaining the auxiliary matrix from the given coefficient matrix.

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 \end{vmatrix} \quad (\text{Matrix 12})$$

The steps to follow in going from the given coefficient matrix, (Matrix 11), to the auxiliary matrix, (Matrix 12), are as follows:

and our final results are of the auxiliary matrix is identical to the first column of the given coefficient matrix. Each element of the

$$B = r_2 c_3 \quad (13)$$

first row of the auxiliary matrix, except the first element, is obtained by dividing the corresponding element of the given coefficient matrix by

$$A = r_1 c_3 - r_1 c_2 \cdot B \quad (14)$$

first element of the coefficient matrix.

The expressions derived by me for evaluating the variances in A and in B are of the form

auxiliary matrix) is equal to the corresponding element of the given matrix (Matrix 11) minus the sum of all the elements in

$$s_A^2 = \left( \frac{r_2 c_2}{R_1 C_1} \right) \cdot s_B^2 - (r_1 c_2) \cdot s_{AB}^2 \quad (15)$$

its row and corresponding elements in the column (In the auxiliary

$$s_B^2 = s_{Y_i}^2 \left( \frac{1}{r_2 c_2} \right) \quad (16)$$

where  $s_{AB}^2$  is the variance in the element to the right of the principal diagonal (of

the auxiliary matrix) is given by a calculation which differs from

$$s_{AB}^2 = (-r_1 c_2) \cdot s_B^2 \quad (17)$$

From the variance in a single  $Y_i$ , in A, and in B, we can evaluate

the variance in our function, equation (2). This is done by applying the general equation for the "Propagation of Errors", equation (1).

To avoid repetition, familiarity with the techniques given in reference 3 is assumed. The formula for evaluating the variance in our function, equation (2), can be determined from the equation (3):



$$s_Y^2 = s_A^2 + 2x_1 s_{AB}^2 + x_1^2 s_B^2 \quad (18)$$

1. Rules for obtaining the auxiliary matrix from the given coefficient matrix

The steps to follow in going from the given coefficient matrix,

(Matrix 11), to the auxiliary matrix, (Matrix 12), are as follows:

(1) The first column of the auxiliary matrix is identical to the first column of the given coefficient matrix. Each element of the first row of the auxiliary matrix, except the first element, is obtained by dividing the corresponding element of the coefficient matrix by the first element of the coefficient matrix.

(2) "Each element on or below the principal diagonal (of the auxiliary matrix) is equal to the corresponding element of the given matrix (Matrix 11) minus the sum of those products of elements in its row and corresponding elements in its column (in the auxiliary matrix) which involve only previously computed elements" (2).

(3) "Each element to the right of the principal diagonal (of the auxiliary matrix) is given by a calculation which differs from rule 3 (rule 2 of this report) only in that there is a final division by its diagonal element (in the auxiliary matrix)" (2).

Suppose we follow the above steps and proceed to go from our coefficient matrix to our auxiliary matrix. Now the coefficient matrix, in abbreviated form, is given as



$R_1 C_1$	$R_1 C_2$	$R_1 C_3$	(Matrix 11)
$R_2 C_1$	$R_2 C_2$	$R_2 C_3$	

Now rule 1 says that the first column of the auxiliary matrix is identical to the first column of the coefficient matrix. Hence,  $R_1 C_1$  and  $R_2 C_1$  appear in the first column of the auxiliary matrix. Rule 1 also says that each element which lies in the first row of the auxiliary matrix, excluding  $R_1 C_1$ , is equal to the corresponding element in the coefficient matrix divided by  $R_1 C_1$ . Hence,  $R_1 C_1$ ,  $R_1 C_2 / R_1 C_1$ , and  $R_1 C_3 / R_1 C_1$  appear in the first row of the auxiliary matrix.

Rule 2 states that any element in the auxiliary matrix which lies on or below the principal diagonal<sup>3/</sup> of the auxiliary matrix

3/ The principal diagonal is composed of those elements which have the same row and column index—i.e.:  $R_1 C_1, R_2 C_2, \dots, R_n C_n$ . The principal diagonal starts with that element in the upper left hand corner and slopes down to the right. In our coefficient matrix, the principal diagonal is made up of  $R_1 C_1$  and  $R_2 C_2$ .

is equal to the corresponding element in the given matrix,  $R_2 C_2$ , minus the sum of those products of elements in its row and corresponding elements in its column,  $R_2 C_1 \cdot R_1 C_2$ . Therefore, from our auxiliary



matrix

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 \end{vmatrix} \quad (\text{Matrix 12})$$

we see from rule 2 that  $r_2 c_2 = R_2 C_2 - R_2 C_1 \cdot r_1 c_2$ .

Finally, rule 3 says that in evaluating an element which lies to the right of the principal diagonal of the auxiliary matrix, we follow step 2 and then divide by the diagonal element. That is,  $r_2 c_3$  is equal to the corresponding element in our coefficient matrix,  $R_2 C_3$ , minus the sum of those products of elements in its row and corresponding elements in its column of the auxiliary matrix,  $R_2 C_1 \cdot r_1 c_3$ , and then all of this is to be divided by the diagonal element of the auxiliary matrix which lies in the same row as  $r_2 c_3$ . Therefore,

$$r_2 c_3 = \frac{R_2 C_3 - R_2 C_1 \cdot r_1 c_3}{r_2 c_2}$$

Now all of the elements which make up our auxiliary matrix have been defined and we proceed to outline the procedure for going from our auxiliary matrix to a set of final results.

## 2. Rules for obtaining the final results from the auxiliary matrix

In going from the auxiliary matrix, (Matrix 12), to the final result, equations (13) and (14), we proceed as follows:

(1) We evaluate our coefficients of equation (2) in reverse order; for example, we evaluate first B and then A.

(2) The last coefficient, B, is numerically equal to the corresponding element in the last column of our auxiliary matrix.



(3) Each of the other coefficients is "...equal to the corresponding element of the last column of the auxiliary matrix minus the sum of those products of elements in its row in the auxiliary matrix and corresponding elements in its column in the final matrix which involve only previously computed elements" (2).

Now suppose we follow the above steps in going from our auxiliary matrix to our final solution. Now the auxiliary matrix, in abbreviated form, is given as

$$\begin{vmatrix} R_1 c_1 & r_1 c_2 & r_1 c_3 \\ R_2 c_1 & r_2 c_2 & r_2 c_3 \end{vmatrix} \quad (\text{Matrix 12})$$

Rule 1 says that the first constant we evaluate is B and the second constant we evaluate is A. Rule 2 says that B is numerically equal to the last element in the last column of the auxiliary matrix. Therefore,  $B = r_2 c_3$ . Rule 3 then says that A is equal to the next to the last element in the last column of the auxiliary matrix ( $r_1 c_3$ ) minus the sum of those products of elements in its row in the auxiliary matrix and corresponding elements in the last column of our final results. Therefore,  $A = r_1 c_3 - r_1 c_2 \cdot B$ .

For curves of higher degree, the following formulas for evaluating coefficients are given along with formulas derived by me for evaluating the above-mentioned errors.

For a function of the kind

$$Y = A + Bx_1 + Cx_2 \quad (19)$$



the method of the auxiliary matrix can be used for the solution of the set of normal equations. The normal equations are:

$$An + B\Sigma x_{1i} + C\Sigma x_{2i} = \Sigma Y_i \quad (19a)$$

$$A\Sigma x_{1i} + B\Sigma x_{1i}^2 + C\Sigma x_{1i} x_{2i} = \Sigma x_{1i} Y_i \quad (19b)$$

$$A\Sigma x_{2i} + B\Sigma x_{1i} x_{2i} + C\Sigma x_{2i}^2 = \Sigma x_{2i} Y_i \quad (19c)$$

Therefore, our coefficient matrix is of the form

$$\begin{vmatrix} n & \Sigma x_{1i} & \Sigma x_{2i} & \Sigma Y_i \\ \Sigma x_{1i} & \Sigma x_{1i}^2 & \Sigma x_{1i} x_{2i} & \Sigma x_{1i} Y_i \\ \Sigma x_{2i} & \Sigma x_{1i} x_{2i} & \Sigma x_{2i}^2 & \Sigma x_{2i} Y_i \end{vmatrix} \quad (\text{Matrix 19d})$$

or, if we use the symbolism R and C to represent the words row and column, respectively, we can abbreviate (Matrix 19d) as

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 & R_1 C_4 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 & R_2 C_4 \\ R_3 C_1 & R_3 C_2 & R_3 C_3 & R_3 C_4 \end{vmatrix} \quad (\text{Matrix 19e})$$

and from the rules cited for obtaining the auxiliary matrix from the given coefficient matrix, we have as our auxiliary matrix<sup>4/</sup>

4/ The relations for obtaining each element of the auxiliary matrix from the given coefficient matrix for third and fourth order matrices, respectively, are given in the appendix of this report.



$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 & r_1 c_4 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 & r_2 c_4 \\ R_3 C_1 & r_3 c_2 & r_3 c_3 & r_3 c_4 \end{vmatrix} \quad (\text{Matrix 19f})$$

and our final result is of the form

$$C = r_3 c_4 \quad (19g)$$

$$B = r_2 c_4 - r_2 c_3 C \quad (19h)$$

$$A = r_1 c_4 - r_1 c_3 \cdot C - r_1 c_2 \cdot B \quad (19i)$$

The variance in a single  $Y_i$  is given as

$$s_{Y_i}^2 = \frac{\sum (Y_{i\text{obs}} - Y_{i\text{cal}})^2}{n - 3} \quad (19j)$$

The error in our function, equation (19), can be evaluated from the expression (3)

$$s_Y^2 = s_A^2 + 2x_1 s_{AB}^2 + x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + 2x_2 s_{AC}^2 + x_2^2 s_C^2 \quad (19k)$$

where

$$s_A^2 = (r_3 c_3 / R_1 C_1) \cdot s_C^2 - (r_1 c_3) \cdot s_{AC}^2 - (r_1 c_2) \cdot s_{AB}^2 \quad (19m)$$

$$s_{AB}^2 = - (r_1 c_3) \cdot s_{BC}^2 - (r_1 c_2) \cdot s_B^2 \quad (19n)$$

$$s_{AC}^2 = - (r_1 c_3) \cdot s_C^2 - (r_1 c_2) \cdot s_{BC}^2 \quad (19o)$$

$$s_B^2 = (r_3 c_3 / r_2 c_2) \cdot s_C^2 - (r_2 c_3) \cdot s_{BC}^2 \quad (19p)$$



$$s_{BC}^2 = - (r_2 c_3) \cdot s_C^2 \quad (19q)$$

$$s_C^2 = s_{Y_i}^2 (1/r_3 c_3) \quad (19r)$$

For an equation of the form

$$Y = A + Bx_1 + Cx_2 + Dx_3 \quad (20)$$

our normal equations are

Proceeding from (Matrix 20e), we can write our auxiliary matrix as

$$An + B\Sigma x_{1i} + C\Sigma x_{2i} + D\Sigma x_{3i} = \Sigma Y_i \quad (20a)$$

$$A\Sigma x_{1i} + B\Sigma x_{1i}^2 + C\Sigma x_{1i} x_{2i} + D\Sigma x_{1i} x_{3i} = \Sigma x_{1i} Y_i \quad (20b)$$

$$A\Sigma x_{2i} + B\Sigma x_{1i} x_{2i} + C\Sigma x_{2i}^2 + D\Sigma x_{2i} x_{3i} = \Sigma x_{2i} Y_i \quad (20c)$$

$$A\Sigma x_{3i} + B\Sigma x_{1i} x_{3i} + C\Sigma x_{2i} x_{3i} + D\Sigma x_{3i}^2 = \Sigma x_{3i} Y_i \quad (20d)$$

Hence, our coefficient matrix is of the form

$$\begin{vmatrix} n & \Sigma x_{1i} & \Sigma x_{2i} & \Sigma x_{3i} & \Sigma Y_i \\ \Sigma x_{1i} & \Sigma x_{1i}^2 & \Sigma x_{1i} x_{2i} & \Sigma x_{1i} x_{3i} & \Sigma x_{1i} Y_i \\ \Sigma x_{2i} & \Sigma x_{1i} x_{2i} & \Sigma x_{2i}^2 & \Sigma x_{2i} x_{3i} & \Sigma x_{2i} Y_i \\ \Sigma x_{3i} & \Sigma x_{1i} x_{3i} & \Sigma x_{2i} x_{3i} & \Sigma x_{3i}^2 & \Sigma x_{3i} Y_i \end{vmatrix} \quad (\text{Matrix 20e})$$



We can write (Matrix 20e) in abbreviated form as

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 & R_1 C_4 & R_1 C_5 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 & R_2 C_4 & R_2 C_5 \\ R_3 C_1 & R_3 C_2 & R_3 C_3 & R_3 C_4 & R_3 C_5 \\ R_4 C_1 & R_4 C_2 & R_4 C_3 & R_4 C_4 & R_4 C_5 \end{vmatrix} \quad (20e)$$

(Matrix 20f)

Proceeding from (Matrix 20f), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 & r_1 c_4 & r_1 c_5 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 & r_2 c_4 & r_2 c_5 \\ R_3 C_1 & r_3 c_2 & r_3 c_3 & r_3 c_4 & r_3 c_5 \\ R_4 C_1 & r_4 c_2 & r_4 c_3 & r_4 c_4 & r_4 c_5 \end{vmatrix} \quad (20g)$$

(Matrix 20g)

and our final result is of the form

$$D = r_4 c_5 \quad (20h)$$

$$C = r_3 c_5 - (r_3 c_4) \cdot D \quad (20i)$$

$$B = r_2 c_5 - (r_2 c_4) \cdot D - (r_2 c_3) \cdot C \quad (20j)$$

$$A = r_1 c_5 - (r_1 c_4) \cdot D - (r_1 c_3) \cdot C - (r_1 c_2) \cdot B \quad (20k)$$

The variance in our function, equation (20), can be determined from the expression (3)



$$s_A^2 + 2x_1 s_{AB}^2 + 2x_2 s_{AC}^2 + 2x_3 s_{AD}^2 \quad (20m)$$

$$s_Y^2 = + x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + 2x_1 x_3 s_{BD}^2 \quad (20m)$$

$$+ x_2^2 s_C^2 + 2x_2 x_3 s_{CD}^2 + x_3^2 s_D^2$$

and of higher degrees and to the standard errors associated with each

where

$$s_{Y_i}^2 = \frac{\sum (Y_{i\text{obs}} - Y_{i\text{cal}})^2}{n - 4} \quad (20n)$$

$$s_{AB}^2 = (r_4 c_4 / R_1 c_1) \cdot s_D^2 - (r_1 c_4) \cdot s_{AD}^2 - (r_1 c_3) \cdot s_{AC}^2 - (r_1 c_2) \cdot s_{AB}^2 \quad (20o)$$

$$s_{AC}^2 = - (r_1 c_4) \cdot s_{BD}^2 - (r_1 c_3) \cdot s_{BC}^2 - (r_1 c_2) \cdot s_B^2 \quad (20p)$$

$$s_{AD}^2 = - (r_1 c_4) \cdot s_D^2 - (r_1 c_3) \cdot s_{CD}^2 - (r_1 c_2) \cdot s_{BD}^2 \quad (20q)$$

$$s_{BC}^2 = - (r_2 c_4) \cdot s_D^2 - (r_2 c_3) \cdot s_{CD}^2 - (r_2 c_2) \cdot s_{BD}^2 \quad (20r)$$

$$s_B^2 = (r_4 c_4 / r_2 c_2) \cdot s_D^2 - (r_2 c_4) \cdot s_{BD}^2 - (r_2 c_3) \cdot s_{BC}^2 \quad (20s)$$

$$s_{CD}^2 = - (r_3 c_4) \cdot s_D^2 - (r_3 c_3) \cdot s_C^2 \quad (20t)$$

$$s_{BD}^2 = - (r_2 c_4) \cdot s_D^2 - (r_2 c_3) \cdot s_{CD}^2 \quad (20u)$$

$$s_C^2 = (r_4 c_4 / r_3 c_3) \cdot s_D^2 - (r_3 c_4) \cdot s_{CD}^2 \quad (20v)$$

$$s_{CD}^2 = - (r_3 c_4) \cdot s_D^2 \quad (20w)$$



$$s_D^2 = s_{Y_i}^2 (1/r_4 c_4) \quad (20x)$$

Attention has been given to functions of the kind

$$Y = 1 + Bx_1 + Cx_2 \quad (21)$$

and of higher degree and to the standard error associated with each coefficient. The normal equations for equation (21) are

$$B \sum x_{1_i}^2 + C \sum x_{1_i} x_{2_i} = (\sum x_{1_i} Y_i - \sum x_{1_i}) \quad (21a)$$

$$B \sum x_{1_i} x_{2_i} + C \sum x_{2_i}^2 = (\sum x_{2_i} Y_i - \sum x_{2_i}) \quad (21b)$$

and our coefficient matrix is of the form

$$\begin{vmatrix} \sum x_{1_i}^2 & \sum x_{1_i} x_{2_i} & (\sum x_{1_i} Y_i - \sum x_{1_i}) \\ \sum x_{1_i} x_{2_i} & \sum x_{2_i}^2 & (\sum x_{2_i} Y_i - \sum x_{2_i}) \end{vmatrix} \quad (\text{Matrix 21c})$$

Writing (Matrix 21c) in abbreviated form, we have

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 \end{vmatrix} \quad (\text{Matrix 21d})$$

as our given coefficient matrix. The auxiliary matrix is given by

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 \end{vmatrix} \quad (\text{Matrix 21e})$$



Thus, our final result is

$$C = r_2 c_3 \quad (21f)$$

$$B = r_1 c_3 - (r_1 c_2) \cdot C \quad (21g)$$

The variance in our function, equation (21), is given by (3)

$$s_Y^2 = x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + x_2^2 s_C^2 \quad (21h)$$

where

$$s_B^2 = (r_2 c_2 / R_1 C_1) \cdot s_C^2 - (r_1 c_2) \cdot s_{BC}^2 \quad (21i)$$

$$s_{BC}^2 = - (r_1 c_2) \cdot s_C^2 \quad (21j)$$

$$s_C^2 = s_{Y_i}^2 (1/r_2 c_2) \quad (21k)$$

and

$$s_{Y_i}^2 = \frac{\sum (Y_{i\text{obs}} - Y_{i\text{cal}})^2}{n - 2} \quad (21m)$$

For the function

$$Y = 1 + Bx_1 + Cx_2 + Dx_3 \quad (22)$$

our normal equations are

$$B \sum x_{1i}^2 + C \sum x_{1i} x_{2i} + D \sum x_{1i} x_{3i} = (\sum x_{1i} Y_i - \sum x_{1i}) \quad (22a)$$

$$B \sum x_{1i} x_{2i} + C \sum x_{2i}^2 + D \sum x_{2i} x_{3i} = (\sum x_{2i} Y_i - \sum x_{2i}) \quad (22b)$$

$$B \sum x_{1i} x_{3i} + C \sum x_{2i} x_{3i} + D \sum x_{3i}^2 = (\sum x_{3i} Y_i - \sum x_{3i}) \quad (22c)$$



From equations (22a), (22b), and (22c), we can write our coefficient matrix as

$$\begin{vmatrix} \Sigma x_1^2_i & \Sigma x_1 x_2_i & \Sigma x_1 x_3_i & (\Sigma x_1 Y_i - \Sigma x_1)_i \\ \Sigma x_1 x_2_i & \Sigma x_2^2_i & \Sigma x_2 x_3_i & (\Sigma x_2 Y_i - \Sigma x_2)_i \\ \Sigma x_1 x_3_i & \Sigma x_2 x_3_i & \Sigma x_3^2_i & (\Sigma x_3 Y_i - \Sigma x_3)_i \end{vmatrix} \quad (\text{Matrix 22d})$$

where

In abbreviated form, (Matrix 22d) is given as

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 & R_1 C_4 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 & R_2 C_4 \\ R_3 C_1 & R_3 C_2 & R_3 C_3 & R_3 C_4 \end{vmatrix} \quad (\text{Matrix 22e})$$

and from (Matrix 22e), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 & r_1 c_4 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 & r_2 c_4 \\ R_3 C_1 & r_3 c_2 & r_3 c_3 & r_3 c_4 \end{vmatrix} \quad (\text{Matrix 22f})$$

and

Hence, our final result is given to be

$$D = r_3 c_4 \quad (22g)$$

Finally, for the solution

$$C = r_2 c_4 - (r_2 c_3) \cdot D \quad (22h)$$

$$B = r_1 c_4 - (r_1 c_3) \cdot D - (r_1 c_2) \cdot C \quad (22i)$$



We can determine the error in our function, equation (22), from the expression (3)

$$s_Y^2 = x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + 2x_1 x_3 s_{BD}^2 + x_2^2 s_C^2 + 2x_2 x_3 s_{CD}^2 + x_3^2 s_D^2 \quad (22j)$$

where

$$s_B^2 = (r_3 c_3 / R_1 c_1) \cdot s_D^2 - (r_1 c_3) \cdot s_{BD}^2 - (r_1 c_2) \cdot s_{BC}^2 \quad (22k)$$

$$s_{BC}^2 = - (r_1 c_3) \cdot s_{CD}^2 - (r_1 c_2) \cdot s_C^2 \quad (22m)$$

$$s_{BD}^2 = - (r_1 c_3) \cdot s_D^2 - (r_1 c_2) \cdot s_{CD}^2 \quad (22n)$$

$$s_C^2 = (r_3 c_3 / r_2 c_2) \cdot s_D^2 - (r_2 c_3) \cdot s_{CD}^2 \quad (22o)$$

$$s_{CD}^2 = - (r_2 c_3) \cdot s_D^2 \quad (22p)$$

$$s_D^2 = s_{Y_i}^2 (1/r_3 c_3) \quad (22q)$$

and

$$s_{Y_i}^2 = \frac{\sum (Y_{i,obs} - Y_{i,cal})^2}{n - 3} \quad (22r)$$

Finally, for the function

$$Y = 1 + Bx_1 + Cx_2 + Dx_3 + Ex_4 \quad (23)$$

we have the set of normal equations

$$B \sum x_{1i}^2 + C \sum x_{1i} x_{2i} + D \sum x_{1i} x_{3i} + E \sum x_{1i} x_{4i} = (\sum x_{1i} Y_i - \sum x_{1i}) \quad (23a)$$



$$B \sum x_1 x_2_i + C \sum x_2^2_i + D \sum x_2 x_3_i + E \sum x_2 x_4_i = (\sum x_2 Y_i - \sum x_2) \quad (23b)$$

$$B \sum x_1 x_3_i + C \sum x_2 x_3_i + D \sum x_3^2_i + E \sum x_3 x_4_i = (\sum x_3 Y_i - \sum x_3) \quad (23c)$$

$$B \sum x_1 x_4_i + C \sum x_2 x_4_i + D \sum x_3 x_4_i + E \sum x_4^2_i = (\sum x_4 Y_i - \sum x_4) \quad (23d)$$

The variations in our function, equation (23), can be determined from from which we can evaluate B, C, D, and E. Our given coefficient matrix, written in abbreviated form, is given as

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 & R_1 C_4 & R_1 C_5 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 & R_2 C_4 & R_2 C_5 \\ R_3 C_1 & R_3 C_2 & R_3 C_3 & R_3 C_4 & R_3 C_5 \\ R_4 C_1 & R_4 C_2 & R_4 C_3 & R_4 C_4 & R_4 C_5 \end{vmatrix} \quad (\text{Matrix 23e})$$

Proceeding from (Matrix 23e), we can write our auxiliary matrix as

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 & r_1 c_4 & r_1 c_5 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 & r_2 c_4 & r_2 c_5 \\ R_3 C_1 & r_3 c_2 & r_3 c_3 & r_3 c_4 & r_3 c_5 \\ R_4 C_1 & r_4 c_2 & r_4 c_3 & r_4 c_4 & r_4 c_5 \end{vmatrix} \quad (\text{Matrix 23f})$$

Hence, from our auxiliary matrix, (Matrix 23f), we have as our final result

$$E = r_4 c_5 \quad (23g)$$



$$D = r_3 c_5 - (r_3 c_4) \cdot E \quad (23h)$$

$$C = r_2 c_5 - (r_2 c_4) \cdot E - (r_2 c_3) \cdot D \quad (23i)$$

$$B = r_1 c_5 - (r_1 c_4) \cdot E - (r_1 c_3) \cdot D - (r_1 c_2) \cdot C \quad (23j)$$

The variance in our function, equation (23), can be determined from the equation (3)

$$x_1^2 s_B^2 + 2x_1 x_2 s_{BC}^2 + 2x_1 x_3 s_{BD}^2$$

$$s_Y^2 = + 2x_1 x_4 s_{BE}^2 + x_2^2 s_C^2 + 2x_2 x_3 s_{CD}^2$$

$$+ 2x_2 x_4 s_{CE}^2 + x_3^2 s_D^2 + 2x_3 x_4 s_{DE}^2 \quad (23k)$$

The method of determining the variance consists of averaging the isothermal variances of the individual terms in terms of a

power series in which pressure or the density and of evaluating

so-called virial coefficients by least squares solution. This report

where

$$s_B^2 = (r_4 c_4 / R_1 c_1) \cdot s_E^2 - (r_1 c_4) \cdot s_{BE}^2 - (r_1 c_3) \cdot s_{BD}^2 - (r_1 c_2) \cdot s_{BC}^2 \quad (23m)$$

$$s_{BC}^2 = - (r_1 c_4) \cdot s_{CE}^2 - (r_1 c_3) \cdot s_{CD}^2 - (r_1 c_2) \cdot s_C^2 \quad (23n)$$

$$s_{BD}^2 = - (r_1 c_4) \cdot s_{DE}^2 - (r_1 c_3) \cdot s_D^2 - (r_1 c_2) \cdot s_{CD}^2 \quad (23o)$$

$$s_{BE}^2 = - (r_1 c_4) \cdot s_E^2 - (r_1 c_3) \cdot s_{DE}^2 - (r_1 c_2) \cdot s_{CE}^2 \quad (23p)$$

$$s_C^2 = (r_4 c_4 / r_2 c_2) \cdot s_E^2 - (r_2 c_4) \cdot s_{CE}^2 - (r_2 c_3) \cdot s_{CD}^2 \quad (23q)$$

$$s_{CD}^2 = - (r_2 c_4) \cdot s_{DE}^2 - (r_2 c_3) \cdot s_D^2 \quad (23r)$$

$$s_{CE}^2 = - (r_2 c_4) \cdot s_E^2 - (r_2 c_3) \cdot s_{DE}^2 \quad (23s)$$



$$s_D^2 = (r_4 c_4 / r_3 c_3) \cdot s_E^2 - (r_3 c_4) \cdot s_{DE}^2 \quad (23t)$$

$$s_{DE}^2 = - (r_3 c_4) \cdot s_D^2 \quad (23u)$$

$$s_E^2 = s_{Y_i}^2 (1/r_4 c_4) \quad (23v)$$

and auxiliary matrix. Next we evaluate all elements in the second column and then all elements in the first row of our auxiliary matrix. We then evaluate all elements which lie in the first row of and auxiliary matrix. Next we evaluate all elements in the second column and then all elements in the first row of and so on until all elements of our auxiliary matrix are defined.

### CONCLUSIONS

The method of treating PVT data on gases consists of expressing the isothermal variation of the PV product of a gas in terms of a power series in either the pressure or the density and of evaluating so-called virial coefficients by least squares solution. This report gives a brief summary of the method of the auxiliary matrix, previously published by Crout, and its application to rational integral functions of one to four degrees, without going into any details of the mathematical background of statistics or into the various approaches to the problem of curve fitting.

Formulas for calculating the standard error in a single measurement, the standard error in each coefficient, and the standard error of the respective functions are given, without proof, and are presented on the basis of unit weight being given to each observed measurement.



## APPENDIX

In evaluating the elements of the auxiliary matrix, it is most convenient to determine these elements in the following order: First, we evaluate all elements which lie in the first column of our auxiliary matrix. We then evaluate all elements which lie in the first row of our auxiliary matrix. Next we evaluate all elements in the second column and then all elements in the second row and so on until all elements of our auxiliary matrix are defined.

Now suppose we have a third order coefficient matrix of the form

$$\begin{vmatrix} R_1 C_1 & R_1 C_2 & R_1 C_3 & R_1 C_4 \\ R_2 C_1 & R_2 C_2 & R_2 C_3 & R_2 C_4 \\ R_3 C_1 & R_3 C_2 & R_3 C_3 & R_3 C_4 \end{vmatrix} \quad (\text{Matrix 19d})$$

and a third order auxiliary matrix of the form

$$\begin{vmatrix} R_1 C_1 & r_1 c_2 & r_1 c_3 & r_1 c_4 \\ R_2 C_1 & r_2 c_2 & r_2 c_3 & r_2 c_4 \\ R_3 C_1 & r_3 c_2 & r_3 c_3 & r_3 c_4 \end{vmatrix} \quad (\text{Matrix 19e})$$

From the rules given on page 10 of this report, the elements of our third order matrix, (Matrix 19e), can be determined from the following relations

$$r_1 c_2 = R_1 C_2 \div R_1 C_1$$

$$r_1 c_3 = R_1 C_3 \div R_1 C_1$$

$$r_3 c_3 = R_3 C_3 - R_3 C_1 \cdot r_1 c_3 - r_3 c_2 \cdot r_2 c_3$$



$$r_1 c_4 = R_1 C_4 \div R_1 C_1$$

$$r_2 c_2 = R_2 C_2 - R_2 C_1 \cdot r_1 c_2$$

$$r_3 c_2 = R_3 C_2 - R_3 C_1 \cdot r_1 c_2$$

$$r_2 c_3 \frac{5/}{5/} = [R_2 C_3 - R_2 C_1 \cdot r_1 c_3] \div r_2 c_2$$

Now we determine the elements of our auxiliary matrix in the same order

$$as cited above - r_2 c_4 = [R_2 C_4 - R_2 C_1 \cdot r_1 c_4] \div r_2 c_2$$

and then second row, and so on until all of the elements are defined.

$$r_3 c_4 = [R_3 C_4 - R_3 C_1 \cdot r_1 c_4 - r_3 c_2 \cdot r_2 c_4] \div r_3 c_3$$

Now from the relations given on page 19b of the report, we see that  
It is to be noted that (Matrix 19e) and (Matrix 22f) are third order  
auxiliary matrices. Therefore, the elements of (Matrix 22f) are determined as outlined above.

Now suppose we have a fourth order coefficient of the form

$R_1 C_1$	$R_1 C_2$	$R_1 C_3$	$R_1 C_4$	$R_1 C_5$	(Matrix 20f)
$R_2 C_1$	$R_2 C_2$	$R_2 C_3$	$R_2 C_4$	$R_2 C_5$	
$R_3 C_1$	$R_3 C_2$	$R_3 C_3$	$R_3 C_4$	$R_3 C_5$	
$R_4 C_1$	$R_4 C_2$	$R_4 C_3$	$R_4 C_4$	$R_4 C_5$	

and a fourth order auxiliary matrix of the form

5/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this particular element can be evaluated by dividing its symmetrically opposite element below the principal diagonal,  $r_3 c_2$ , by the diagonal element which lies in the same row as  $r_2 c_3$ . That is,  $r_2 c_3 = r_3 c_2 \div r_2 c_2$ . This lies to the same row as  $r_2 c_3$ . That is,



$R_1 C_1$	$r_1 c_2$	$r_1 c_3$	$r_1 c_4$	$r_1 c_5$	
$R_2 C_1$	$r_2 c_2$	$r_2 c_3$	$r_2 c_4$	$r_2 c_5$	
$R_3 C_1$	$r_3 c_2$	$r_3 c_3$	$r_3 c_4$	$r_3 c_5$	
$R_4 C_1$	$r_4 c_2$	$r_4 c_3$	$r_4 c_4$	$r_4 c_5$	

Now we determine the elements of our auxiliary matrix in the same order as cited above — i.e., first column and then first row ; second column and then second row, and so on until all of the elements are defined.

Now from the rules given on page 10 of this report, we see that the elements of (Matrix 20g) can be evaluated from the following relations

$$r_1 c_2 = R_1 C_2 \div R_1 C_1$$

$$r_1 c_3 = R_1 C_3 \div R_1 C_1$$

$$r_1 c_4 = R_1 C_4 \div R_1 C_1$$

$$r_1 c_5 = R_1 C_5 \div R_1 C_1$$

7/ Since our auxiliary  $r_2 c_2 = R_2 C_2 - R_2 C_1 \cdot r_1 c_2$

disposal, then this can be evaluated by dividing its

symmetrically opposite element below the principal diagonal.

$$r_4 c_2 = R_4 C_2 - R_4 C_1 \cdot r_1 c_2$$

$r_4 c_2$ , by the diagonal element which lies in the same row as

$$r_2 c_2. \text{ That is, } r_2 c_3^{6/} = [R_2 C_3 - R_2 C_1 \cdot r_1 c_3] \div r_2 c_2$$

8/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this particular element can be evaluated by dividing its symmetrically opposite element below the principal diagonal,  $r_3 c_2$ , by the diagonal element which lies in the same row as  $r_2 c_3$ . That is,

$$r_2 c_3 = r_3 c_2 \div r_2 c_2.$$



$$r_2 c_4 \frac{7/}{7/} = [R_2 c_4 - R_2 c_1 \cdot r_1 c_4] \div r_2 c_2$$

$$r_2 c_5 = [R_2 c_5 - R_2 c_1 \cdot r_1 c_5] \div r_2 c_2$$

$$r_3 c_3 = R_3 c_3 - R_3 c_1 \cdot r_1 c_3 - r_3 c_2 \cdot r_2 c_3$$

$$r_4 c_3 = R_4 c_3 - R_4 c_1 \cdot r_1 c_3 - r_4 c_2 \cdot r_2 c_3$$

$$r_3 c_4 \frac{8/}{8/} = [R_3 c_4 - R_3 c_1 \cdot r_1 c_4 - r_3 c_2 \cdot r_2 c_4] \div r_3 c_3$$

$$r_3 c_5 = [R_3 c_5 - R_3 c_1 \cdot r_1 c_5 - r_3 c_2 \cdot r_2 c_5] \div r_3 c_3$$

$$r_4 c_4 = R_4 c_4 - R_4 c_1 \cdot r_1 c_4 - r_4 c_2 \cdot r_2 c_4 - r_4 c_3 \cdot r_3 c_4$$

$$r_4 c_5 = [R_4 c_5 - R_4 c_1 \cdot r_1 c_5 - r_4 c_2 \cdot r_2 c_5 - r_4 c_3 \cdot r_3 c_5] \div r_4 c_4$$

It is to be noted that (Matrix 20g) and (Matrix 23f) are fourth order auxiliary matrices. Therefore, the elements of (Matrix 23f) are determined as outlined above.

7/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this element can be determined by dividing its symmetrically opposite element below the principal diagonal,  $r_4 c_2$ , by the diagonal element which lies in the same row as  $r_2 c_4$ . That is,  $r_2 c_4 = r_4 c_2 \div r_2 c_2$ .

8/ Since our auxiliary matrix is symmetrical about the principal diagonal, then this element can be determined by dividing its symmetrically opposite element below the principal diagonal,  $r_4 c_3$ , by the diagonal element which lies in the same row as  $r_3 c_4$ . That is,  $r_3 c_4 = r_4 c_3 \div r_3 c_3$ .



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